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UNIVERSITY OF HAWAI'I

FINAL TECHNICAL REPORT

Reporting Period: 15 June 2007 through 30 April 2008

**Naval Research Laboratory
Award No. N00173-07-2-C004 Mod. P0002**

Combustion of Advanced Tactical Fuels Utilizing Boron Nanoparticles

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ABSTRACT

The design of high-energy-content synthetic fuels is an area of significant interest to the U.S. Department of Defense. Toward this end, the Naval Research Laboratory (NRL) has initiated an RD&D project to investigate the addition of coated boron nanoparticles to liquid fuels for gas turbine combustion applications. The Hawaii Natural Energy Institute (HNEI) of the University of Hawaii is collaborating with NRL on this project. HNEI is focusing on the conduct of experiments in benchtop burners with simple flow-reaction geometries to investigate fundamental multi-component/phase droplet ignition, burnout, and emissions phenomena. Both single droplets and group burning will be explored and results will be applied toward the development of combustion models and the interpretation of data obtained in more complex flame geometries. This Final Technical Report summarizes the activities undertaken at HNEI during the initial 10.5 months of the project, when it was supported via an award from NRL. The project currently is continuing under direct funding from the Office of Naval Research (ONR).

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EXECUTIVE SUMMARY

The availability of acceptable fuels for military operations is an area of growing concern to the Department of Defense (DoD). There are indications of a policy shift in the U.S. toward the production and storage of transportation fuels that are not appropriate for certain DoD applications (e.g., natural gas, ethanol, etc.). DARPA/TTO has sponsored a number of recent workshops to explore this issue. One of the primary outcomes of these workshops was to recognize the need to augment the energy content of conventional and future synthetic fuels. It was concluded that one possible approach to accomplish this is the addition of boron nanoparticles to liquid fuels.

In order to assess the feasibility of boron nanoparticles as an energy additive, NRL has initiated an exploratory study in cooperation with the University of Utah and HNEI. Benchtop laboratory experiments will be conducted by HNEI to examine the burning of single droplets and dilute droplet ensembles of multi-component fuels comprising mixtures of conventional liquid fuels and solid boron nanoparticles in simple flow-reaction geometries. Data from these experiments will be applied to the development and testing of submodels of droplet burning phenomena that can be incorporated into flame simulation codes to predict performance and emissions characteristics of gas turbine combustors employing the multi-component fuel. The specific objectives are:

1. Determine the effect of fuel properties including nanoparticle loading and coatings on droplet burning rates.
2. Investigate the mechanism of oxidation of the solid (boron) phase.
3. Develop submodels of single droplet and group burning phenomena for the multi-component fuel.

This project was transferred from NRL to ONR in February 2008 and is continuing. Technical accomplishments by HNEI during the period of performance of the Cooperative Agreement between NRL and UH (15 June 2007 and 30 April 2008) included: 1) development of protocols and facilities for the safe handling, use, and disposal of boron nanoparticles including a new laboratory exhaust system and the procurement of protective suits and supplied-air respirators; 2) assembly, testing, and upgrading the PDPA instrument used to monitor the size and velocity of burning fuel droplets; and 3) initiated the design, procurement, and fabrication of the burner and controls for the group combustion experiments. Experiments and modeling activities will be pursued and reported in the future under the continuing ONR grant.

I TECHNICAL RATIONALE

The availability of acceptable fuels for military operations is an area of growing concern to the Department of Defense (DoD). There are indications of a policy shift in the U.S. toward the production and storage of transportation fuels that are not appropriate for certain DoD applications (e.g., natural gas, ethanol, etc.). DARPA/TTO has sponsored a number of recent workshops to explore this issue. One of the primary outcomes of these workshops was to recognize the need to augment the energy content of conventional and future synthetic fuels. It was concluded that one possible approach to accomplish this is the addition of boron nanoparticles to liquid fuels.

In order to assess the feasibility of boron nanoparticles as an energy additive, NRL has initiated an exploratory study. Issues to be investigated include:

1. Optimization of boron particle size and concentration for maximum energy and combustion efficiency.
2. Which boron compound offers the highest energy density?
3. Which nanoparticle coating yields the best combination of boron stability and efficient combustion?
4. What are the most promising additives/nanoparticle coatings to increase the energy density and control volatility?
5. The suitability of different liquid fuels for utilization with boron nanoparticles.
6. How does the nanoparticle burn in a slurry and what are the products of combustion?
7. How do reaction products vary as combustion conditions change?
8. The effects of the boron additive on ignition, stability, and radiative transfer.
9. Development of models to simulate scalar and momentum fields in the flame zone and post flame gases of boron nanoparticle combustion.

HNEI is collaborating with NRL on topics 6 through 9 above through the conduct of laboratory experiments and modeling activities.

II PROJECT DESCRIPTION

Benchtop laboratory experiments will be conducted by HNEI to examine the burning of single droplets and dilute droplet ensembles of multi-component fuels comprising mixtures of conventional liquid fuels and solid boron nanoparticles in simple flow-reaction geometries. Data from these experiments will be applied to the development and testing of submodels of droplet burning phenomena that can be incorporated into flame simulation codes to predict performance and emissions characteristics of gas turbine combustors employing the multi-component fuel. The specific objectives are:

1. Determine the effect of fuel properties including nanoparticle loading and coatings on droplet burning rates.
2. Investigate the mechanism of oxidation of the solid (boron) phase.

3. Develop submodels of single droplet and group burning phenomena for the multi-component fuel.

The research program will comprise three Tasks:

TASK 1. Single Droplet Combustion Experiments

The burning rates of single droplets suspended by a fine wire thermocouple or silica fiber in an oxidizing atmosphere will be monitored using high resolution video imaging techniques. The control in these tests will be droplets of conventional liquid fuels, probably JP-5. The primary experimental parameters will be boron particle loading, particle size, and particle coating.

TASK 2. Group Burning Experiments

Group burning phenomena will be investigated. A dilute monodispersed ensemble of droplets will be combusted in a simple flow geometry. A shroud flame will be employed to ignite and sustain the combustion of the droplets. A Phase Doppler Particle Analyzer (PDPA) will track the evolution of burning fuel droplet size. The same controls will be employed as in Task 1. Experimental parameters also will be the same, with the addition of fuel droplet size.

TASK 3. Analysis of Results and Modeling

Data collected in Tasks 1 and 2 will be analyzed on the basis of prevailing droplet combustion theory. Submodels that describe the burning characteristics of droplets of multi-component fuels will be developed and tested.

III TECHNICAL ACCOMPLISHMENTS

The Cooperative Agreement between NRL and UH was fully executed at the end of June 2007 and work commenced shortly thereafter. In February 2008, the project was transferred from NRL to ONR. The associated ONR Grant No. N00014-08-1-0375 to UH was executed on 26 February 2008, retroactive to 4 January 2008. The project currently is continuing under direct funding from ONR. In April 2009, the end date of the NRL Cooperative Agreement was subsequently changed from 14 June 2010 to 30 April 2008.

This Section reports technical accomplishments by HNEI during the final (modified) period of performance of NRL Cooperative Agreement No. N00173-07-2-C004 that extends from 15 June 2007 through 30 April 2008. It should be noted that the investigation has continued after 30 April 2008, so that information presented here does not provide a final accounting of the project results, but rather summarizes the initial steps taken to design and assemble the experimental facilities.

Technical progress made between 15 June 2007 and 30 April 2008 included: 1) development of protocols and facilities for the safe handling, use, and disposal of boron nanoparticles including a new laboratory exhaust system and the procurement of protective suits and supplied-air respirators; 2) assembly, testing, and upgrading the PDPA instrument used to monitor the size and velocity of burning fuel droplets; and 3) initiated the design, procurement, and fabrication of the burner and controls for the group combustion experiments.

Nanomaterials may pose environmental, health, and safety (EHS) hazards. A review of the literature was conducted which revealed that, to date, nanomaterial EHS studies are limited and that no standards have been established for their safe handling, use, and disposal. In the U.S., the National Institute for Occupational Safety and Health (NIOSH) has assumed the lead in conducting research on this topic and disseminating results to the public (<http://www.cdc.gov/niosh/topics/nanotech/safenano/>). In the absence of federal regulations, NIOSH has proposed interim guidelines for working with nanomaterials. These guidelines, supplemented by additional recommendations by other institutions of higher education and industry, have been adopted for this project. We believe that the approach taken, while perhaps overly conservative, will ensure that the health and safety of participating personnel and the community are not jeopardized. Toward this end, a new laboratory exhaust system has been designed to minimize exposure to the nanoparticles. Construction of the system (which is being paid for by UH) is scheduled for the fall of 2008. Biological/chemical hazard protection suits and supplied-air respirators also have been procured.

Design, procurement, fabrication, and testing of the experimental facilities that will be employed in Tasks 1 and 2 have been initiated. Work completed includes:

- Re-assembly and testing of the PDPA that was decommissioned and stored in 2005, including replacement of the air-cooled Argon-ion laser.
- Development of the burner and controls for the droplet group combustion experiments.

The single-color PDPA is capable of performing simultaneous measurements of size and one component of velocity of evaporating and burning fuel droplets. In the planned experiments, the optical measurement volume of the PDPA will be fixed in space above the burner. The burner will be mounted on a two-dimensional traverse and moved relative to the PDPA sample volume to map the distributions of droplet size and velocity in the flame. Figure 1 presents a photograph that shows the primary optical components of the PDPA. A rebuilt Argon-ion laser with a maximum power output of >100 mW at 514 nm was procured and tested with the PDPA. The system appears to be working well.

The burner for the droplet group combustion experiments was designed to operate in both diffusion and premixed flame modes. Near monodispersions of liquid fuel droplets will be fed into the burner plenum from a vibrating orifice aerosol generator and mixed with oxidizers, other gaseous fuels, and inert gases. A range of combustion stoichiometries and approach velocities can be examined. The burner was fabricated at UH and has been assembled and tested. Figure 2 presents a photograph of the burner mounted on the two-dimensional translation stage. A premixed flame is shown in which the fuel comprises a mixture of ethanol droplets and methane gas. Laboratory grade dry air is used as the oxidizer. The flame remained stable under a wide range of operating conditions.



Figure 1. PDPA components. The air-cooled argon laser, fiber drive, and transmitter are seen in the upper left corner of the photograph. The optical receiver unit is visible at the left edge of the picture.



Figure 2. Photograph of the burner being tested with a premixed ethanol/methane/air flame.

Conduct of experiments and associated modeling efforts will be pursued under funding from ONR and will be reported in the future.